At *p*H 10 there appeared a solid phase which was shown by analysis to contain no nitrogen. This white, flocculent precipitate was undoubtedly zinc hydroxide. The diffusion current values at this *p*H increase with increasing hydrazine concentration until complete dissolution of the precipitate is indicated by the limiting value of the diffusion current. Thus at hydrazine concentrations of 0.1, 0.2, 0.4, 0.8, 1.0 and 2.0 the diffusion current values were, respectively, 0.20, 0.60, 1.20, 2.44, 2.94 and 3.12 microamperes.

Since, for the same concentration of free hydrazine, the half-wave potentials at *p*H 10 are more negative than those at *p*H 9, it is believed that hydroxo-hydrazine species exist in solution in equilibrium with zinc hydroxide. The limiting slope of the plot of $E_{1/2}$ *versus* log $[N_2H_4]$ (*p*H 10) has a value of about 0.08, indicating that there are probably two or three hydrazine molecules coördinated to the central zinc ion. In addition, the half-wave potential data indicate that at least one hydroxyl group is also coördinated. The existence of the cationic complexes, $[Zn(N_2H_4)_3(OH)]^+$ or $[Zn(N_2H_4)_2(H_2O)(OH)]^+$, appears more probable than that of the neutral species, $[Zn(N_2H_4)_2(OH)_2]$, since the latter would probably be insoluble. As the concentration of excess free hydrazine is decreased, water gradually replaces the remaining hydrazine molecules. The replacement of the last hydrazine molecule is accompanied by the addition of another hydroxyl group, and ultimately all of the zinc is precipitated as the hydroxide.

The logarithms of the successive formation constants (as distinguished from over-all formation constants) by the polarographic technique are approximately 3.4, 0.3, 0.1 and 0.1, whereas 2.8, 1.8, 1.3 and 0.8 were obtained by Schwarzenbach and Zobist[11] from *p*H measurements. These two sets of data are not easily compared, and each is probably valid only for the system from which it was derived. Our values for K_1, K_2, K_3 and K_4 were obtained under conditions quite different from those used by Schwarzenbach and Zobist.[11] The most striking difference is that the polarographic technique involves from 20–600-fold excess free hydrazine, whereas the method of *p*H measurements involves only 2.5-fold excess, under which condition the percentage of lower complexes is greatest. Both methods neglect activity coefficients, and both involve unknown liquid junction potentials which are specific for each system.

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URBANA, ILLINOIS

[CONTRIBUTION FROM THE AVERY LABORATORY OF THE UNIVERSITY OF NEBRASKA]

Polarographic Study of Several *cis* and *trans* Coördination Compounds of Cobalt[1]

BY HENRY F. HOLTZCLAW, JR., AND DAVID P. SHEETZ[2]

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Polarographic reductions were made on several pairs of *cis* and *trans* coördination compounds of cobalt. In the presence of supporting electrolyte, the *cis* isomer was found to exhibit a more positive half-wave potential than the corresponding *trans* isomer for compounds containing negative groups on two of the coördination positions and neutral groups on the other four. For compounds with only one or no negative groups, the *cis* isomers showed no trend toward more positive half-wave potentials. Two distinct polarographic waves for the reduction step Co(III) to Co(II) were noted for several compounds. A postulate is proposed for this phenomenon. Three of the *cis–trans* pairs were also reduced polarographically in the absence of supporting electrolyte, and the limiting currents were compared.

Methods for distinguishing between *cis* and *trans* isomers of inorganic coördination compounds in solution are limited. Recently, Basolo[3] has used the spectrophotometer to study differences in absorption spectra of *cis* and *trans* isomers of certain coördination compounds in solution. A recent paper from this Laboratory[4] reported a polarographic study of *cis*- and *trans*-dinitrotetramminecobalt(III) chloride which showed that the half-wave potential for the *cis* isomer is considerably more positive than that for the *trans*. This suggested that the polarograph might be adapted to a general study of other *cis* and *trans* inorganic coördination compounds. The object of this investigation is to study several groups of *cis* and *trans* isomers of cobalt coördination compounds polarographically to determine whether consistent differences exist between isomeric pairs.

Experimental

Apparatus.—A Sargent Model XXI Polarograph was used with a cell of the type described by Lingane and Kolthoff.[5] Nitrogen, purified of oxygen by means of a vanadyl sulfate column,[6] was bubbled through the cell solution prior to each electrolysis. The potentials of the dropping mercury electrode during electrolysis were measured against an external saturated calomel electrode by means of a standard potentiometer circuit. Cell temperature was maintained at 25.0 ± 0.1° by means of a water thermostat. Reversibility of the electrode reactions was tested by determining the slopes of the plots of log $i/(i_d - i)$ *versus* potential. Half-wave potentials were taken from the logarithmic plots. Each solution for electrolysis was made fresh from the dry cobalt complex before use.

Preparation of Compounds. 1. ***cis*- and *trans*-Dinitrotetramminecobalt (III) Chloride.**—These salts had previously

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[1] Abstracted from the Ph.D. Thesis of David P. Sheetz, July, 1952, University of Nebraska. Presented at the 123rd Meeting of the American Chemical Society, Los Angeles, Calif., March 16, 1953.

[2] Eastman Kodak Fellow, 1951–1952.

[3] F. Basolo, THIS JOURNAL, **72**, 4393 (1950).

[4] H. F. Holtzclaw, Jr., *ibid.*, **73**, 1821 (1951).

[5] J. J. Lingane and I. M. Kolthoff, *ibid.*, **61**, 825 (1939).

[6] L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

been prepared and tested in our laboratory by the method of Biltz and Biltz.[7]

2. ***cis*-Dinitrobisethylenediaminecobalt(III) Nitrate. Method (a)**.—Werner's method[8] starting with potassium hexanitrocobaltate(III) was followed closely with special attention required to initiate the reaction at a temperature around 70–80°.[9] The product was recrystallized once from warm water (60°) and dried in air.

Anal. Calcd. for $[Co(en)_2(NO_2)_2]NO_3$: Co, 17.7. Found: Co, 17.8.

Method (b).—The method of Werner and Gerb[10] starting with *trans*-dichlorobisethylenediaminecobalt(III) chloride[11] was used. The product was recrystallized once from water at 60°.

3. ***trans*-Dinitrobisethylenediaminecobalt(III) Nitrate. Method (a)**.—The method of Werner and Humphrey,[8,12] involving conversion of the *cis* isomer by heat was used. The product was recrystallized once from hot water and dried.

Method (b).—The method of Gerb[13] was used to convert *trans*-dichlorobisethylenediaminecobalt(III) chloride[11] to *trans*-dinitrobisethylenediaminecobalt(III) nitrate with sodium nitrite.

Anal. Calcd. for $[Co(en)_2(NO_2)_2]NO_3$: Co, 17.7. Found: Co, 17.6.

Method (c).—A new method[9] was developed which depends upon oxidation of cobalt(II) to cobalt(III) in the presence of sodium nitrite, ethylenediamine and nitric acid, and which provided a yield of 84%.

Anal. Calcd. for $[Co(en)_2(NO_2)_2]NO_3$: Co, 17.7; N, 29.44. Found: Co, 17.5; N, 29.52.

4. ***cis*-Nitroisothiocyanatobisethylenediaminecobalt(III) Chloride Monohydrate**.—The method of Werner[14] was followed closely. The product was recrystallized several times from 30% acetic acid solution, washed with 95% ethanol, and dried in air.

Anal. Calcd. for $[Co(en)_2(NCS)(NO_2)]Cl{\cdot}H_2O$: Co, 17.5. Found: Co, 17.4.

5. ***trans*-Nitroisothiocyanatobisethylenediaminecobalt(III) Chloride Monohydrate**.—The procedure of Werner[15,16] was followed except for slight modification in proportions of reactants. Ten grams of *trans*-chloronitrobisethylenediaminecobalt(III) nitrate, $[Co(en)_2(NO_2)Cl]NO_3{\cdot}HNO_3$, made from *trans*-dinitrobisethylenediaminecobalt(III) nitrate, was dissolved in 150 ml. of water with gentle heating, and 9 g. of solid potassium thiocyanate was added during the preparation of *trans*-nitroisothiocyanatobisethylenediaminecobalt(III) thiocyanate. Nine grams of this compound was gently heated with 25 ml. of concd. hydrochloric acid in the conversion to *trans*-nitroisothiocyanatobisethylenediaminecobalt(III) chloride monohydrate. After removal of free sulfur, the brown crystalline product was precipitated with 95% ethanol in an ice–salt-bath, recrystallized once from water, and dried in air.

Anal. Calcd. for $[Co(en)_2(NCS)(NO_2)]Cl{\cdot}H_2O$: Co, 17.5. Found: Co, 17.7.

6. ***cis*-Bisethylenediaminediamminecobalt(III) Iodide**.[17,18]—Five grams of *trans*-dibromobisethylenediaminecobalt(III) bromide, obtained by treating *trans*-dichlorobisethylenediaminecobalt(III) chloride[11] with an excess of concd. hydrobromic acid and evaporating the resulting mixture on a steam-bath, were covered over with about 40 ml. of liquid ammonia, whereupon most of the salt dissolved. Evaporation of the red-brown solution to dryness produced a residue which was then dissolved in 50 ml. of water. The resulting solution was neutralized with acetic acid. Three grams of sodium dithionate was added with stirring and the mixture allowed to stand for 30 min., whereupon yellow *trans*-bisethylenediaminediamminecobalt(III) dithionate precipitated and was removed. The filtrate, when mixed with a solution of 10 g. of iodine in 12 ml. of concd. hydriodic acid, produced a heavy dark grey precipitate which was separated and triturated, without drying, with a few drops of water and an excess of sodium thiosulfate. The yellow slurry thus obtained was taken up in 15 ml. of water and filtered to give a clear yellow filtrate. Addition of excess potassium iodide produced yellow-orange crystals of *cis*-bisethylenediaminediamminecobalt(III) iodide, which were recrystallized four times by dissolving in water and reprecipitating with excess potassium iodide. The product was washed with 95% ethanol and dried in air.

Anal. Calcd. for $[Co(en)_2(NH_3)_2]I_3$: Co, 9.9. Found: Co, 9.8.

7. ***trans*-Bisethylenediaminediamminecobalt(III) Chloride Monohydrate**.—The method of Werner[19] was followed. Eleven grams of *trans*-bisisothiocyanatobisethylenediaminecobalt(III) thiocyanate, prepared by the method of Werner,[20] were dissolved, with heating, in a solution of 35 ml. of concd. hydrochloric acid and 380 ml. of water. Chlorine was bubbled through the boiling solution for 20 min., after which the solution was reduced to about 70 ml. volume by evaporation on a steam-bath and allowed to stand overnight. The orange-yellow crystals of impure bisethylenediaminediamminecobalt(III) chloride were combined with an additional crop obtained by further evaporation of the filtrate to about 35 ml. and were purified by solution in 50 ml. of water with warming, addition of 10 ml. of concd. hydrochloric acid, and slow addition of ethanol until the yellow powder which formed just dissolved on stirring. Yellow crystals of *trans*-bisethylenediaminediamminecobalt(III) chloride monohydrate precipitated overnight and were recrystallized once from warm water (35°) and dried in air; m.p. 238–239°.

8. ***cis*-Nitrobisethylenediamineamminecobalt(III) Bromide**.—*cis*-Aquobisethylenediamineamminecobalt(III) bromide was prepared by the method of Werner[21] from *cis*-chlorobisethylenediamineamminecobalt(III) chloride which in turn was made by triturating *trans*-dichlorobisethylenediaminecobalt(III) chloride[11] with concd. aqueous ammonia. *cis*-Nitrobisethylenediamineamminecobalt(III) bromide was prepared from *cis*-aquobisethylenediamineamminecobalt(III) bromide by following carefully the method of Werner.[22] The orange-yellow product was recrystallized once from water at 40°.

Anal. Calcd. for $[Co(en)_2(NH_3)(NO_2)]Br_2$: Co, 14.7. Found: Co, 15.1.

9. ***trans*-Nitrobisethylenediamineamminecobalt(III) Nitrate**.—*trans*-Nitratonitrobisethylenediaminecobalt(III) nitrate was prepared from *trans*-dinitrobisethylenediaminecobalt(III) nitrate and reacted with liquid ammonia according to the procedure of Werner[23] to produce *trans*-nitrobisethylenediamineamminecobalt(III) nitrate contaminated with yellow crystals of the *trans* dinitro salt. Separation was effected by swirling with 95% ethanol and pouring off the suspended yellow dinitro compound. The brown crystals of *trans*-nitrobisethylenediamineamminecobalt(III) nitrate which remained were recrystallized once from water and dried.

Anal. Calcd. for $[Co(en)_2(NH_3)(NO_2)](NO_3)_2$: Co, 16.1. Found: Co, 16.3.

10. ***cis*-Isothiocyanatobisethylenediamineamminecobalt(III) Thiocyanate**.—Werner's method[24] was followed carefully in converting *trans*-dichlorobisethylenediaminecobalt(III) chloride to *cis*-chloroisothiocyanatobisethylenediaminecobalt(III) chloride from which the *cis*-isothiocyanatobisethylenediamineamminecobalt(III) thiocyanate was obtained. The product, recrystallized twice from very small volumes of water and dried, was contaminated with potassium thiocyanate. Its extreme solubility made further purification impractical.

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[10] A. Werner and L. Gerb, *Ber.*, **34**, 1739 (1901).

[11] J. C. Bailar, Jr., ref. 9, Vol. II, 1946, p. 222.

[12] A. Werner, *Ann.*, **386**, 1 (1912); see p. 248.

[13] L. Gerb, *J. Russ. Phys.-Chem. Soc.*, **37**, 43 (1905).

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[16] Ref. 12, p. 240.

[17] S. Jörgensen, *J. prakt. Chem.*, [2], **41**, 440 (1890); see p. 442.

[18] Ref. 12, p. 204.

[19] A. Werner, *Ann.*, **351**, 65 (1907); see p. 71.

[20] A. Werner, *Z. anorg. u. allgem. Chem.*, **22**, 91 (1900); see pp. 125, 141.

[21] Ref. 12, pp. 165, 185, 192.

[22] Ref. 12, p. 218.

[23] Ref. 12, pp. 224, 241.

[24] Ref. 12, pp. 134, 139, 206.

11. ***trans*-Isothiocyanatobisethylenediamineamminecobalt(III) Thiocyanate.**—*trans*-Chloroisothiocyanatobisethylenediaminecobalt(III) thiocyanate, obtained in the synthesis of *cis*-isothiocyanatobisethylenediamineamminecobalt(III) thiocyanate, was converted to *trans*-isothiocyanatobisethylenediamineamminecobalt(III) thiocyanate by the method of Werner.[24] The product was recrystallized once from water, washed with 95% ethanol, and dried in air.

Anal. Calcd. for $[Co(en)_2(NH_3)(NCS)](CNS)_2$: Co, 16.0. Found: Co, 16.1.

12. **α-Triglycinecobalt(III) Dihydrate.**—The essentials of the method of Ley and Winkler[25] were followed. Twenty grams of cobalt(III) hydroxide, prepared by passing chlorine into an alkaline slurry of cobalt(II) hydroxide, was added to 25 g. of glycine dissolved in 100 ml. of water. The mixture was boiled for five hours, replacing water lost by evaporation, and was filtered hot. The filtrate precipitated purple crystals of triglycinecobalt(III) dihydrate while standing overnight in a vacuum desiccator over concd. sulfuric acid. The product was purified by two recrystallizations from water.

Anal. Calcd. for $Co(CH_2NH_2COO)_3 \cdot 2H_2O$: Co, 18.5. Found: Co, 18.2.

13. **β-Triglycinecobalt(III) Monohydrate.**[25]—The residue from the first filtration in Procedure (12) was suspended in 100 ml. of water and the mixture heated on a steam-bath. Sulfur dioxide was then bubbled through until the black cobalt(III) hydroxide had dissolved. The red-violet residue remaining was triturated with portions of hot water until the supernatant liquid possessed no violet coloration, whereupon the residue, triglycinecobalt(III) monohydrate, was filtered and dried in air.

Anal. Calcd. for $Co(CH_2NH_2COO)_3 \cdot H_2O$: Co, 19.7. Found: Co, 19.7.

14. **α-Trisalaninecobalt(III).**[26]—The general method was the same as that described for the triglycine derivative in Procedure (12), adding 20 g. of cobalt(III) hydroxide to 30 g. of *dl*-alanine in 200 ml. of water. The filtrate was evaporated to half its volume before allowing it to stand overnight. The product was washed with water, 95% ethanol and diethyl ether, and dried in air.

Anal. Calcd. for $Co(CH_3CHNH_2COO)_3$: Co, 18.3. Found: Co, 18.6.

15. **β-Trisalaninecobalt(III).**[26]—The method was similar to that described for the corresponding triglycine derivative in Procedure (13), using, however, 150 ml. to suspend the residue. The product was dissolved in 12 *M* sulfuric acid and reprecipitated by addition of water, then removed by filtration, washed with water and dried in air.

Anal. Calcd. for $Co(CH_3CHNH_2COO)_3$: Co, 18.3. Found: Co, 18.2.

Results and Discussion

The present investigation is concerned only with the polarographic reduction of Co(III) to Co(II). Slopes of the log plots indicate irreversible reduction throughout.

An examination of Table I shows that several of the ethylenediamine compounds studied gave rise to two distinct polarographic waves for the reduction step Co(III) to Co(II). Figures 1, 2 and 3 show typical polarograms. This double wave in very dilute solution (0.001 *M*) is thought to be due to an aquation process in which one or more of the coördinated groups, other than ethylenediamine, are replaced in some of the molecules by water, resulting in an equilibrium between the molecules of the aquated complex and molecules of the original species. Such an equilibrium condition could account for the two polarographic waves obtained since the two reducible species might be expected to have different half-wave potentials. This postulate is advanced for the following reasons.

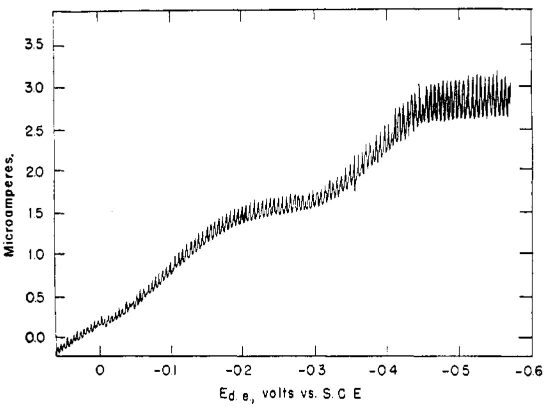

Fig. 1.—Co(III) to Co(II) reduction of 0.001 *M* *trans*-isothiocyanatobisethylenediamineamminecobalt(III) thiocyanate in 0.1 *M* potassium chloride; one drop 0.1% methyl red added to 25 ml. solution. (Solution about two hours old).

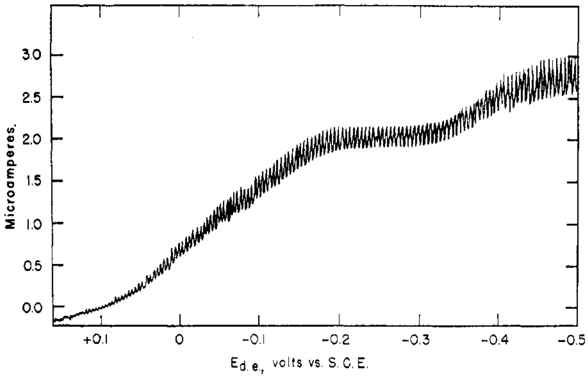

Fig. 2.—Co(III) to Co(II) reduction of 0.001 *M* *cis*-nitroisothiocyanatobisethylenediaminecobalt(III) chloride monohydrate in 0.1 *M* potassium nitrate; two drops of 0.1% methyl red added to 100 ml. of solution.

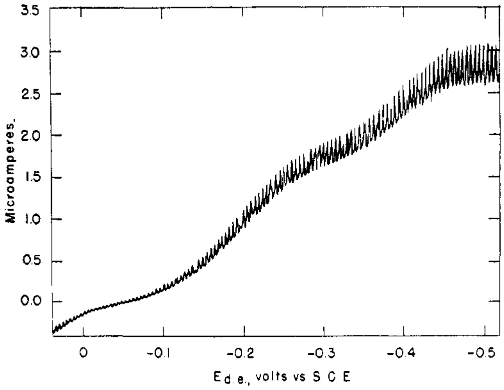

Fig. 3.—Co(III) to Co(II) reduction of 0.001 *M* *trans*-nitrobisethylenediamineamminecobalt(III) nitrate in 0.1 *M* potassium chloride and 0.002 *M* sodium bromide.

(1) The second of the two waves consistently appeared at about −0.40 v. *versus* the saturated calomel electrode (S.C.E.). (2) *cis*-Chloronitrobisethylenediaminecobalt(III) nitrate, known to aquate in dilute solution, exhibited two waves the first of which was sufficiently positive to merge with the anodic mercury wave but the second of which was well characterized and had a half-wave po-

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[25] H. Ley and H. Winkler, *Ber.*, **42**, 3894 (1909).

[26] H. Ley and H. Winkler, *ibid.*, **45**, 372 (1912).

TABLE I

POLAROGRAPHIC REDUCTION OF COBALT COÖRDINATION COMPOUNDS

0.1 M potassium chloride as supporting electrolyte unless otherwise noted; concn. reducible ion, 0.001 M; m = 1.397 milligrams per second; temperature = 25.0 ± 0.1°; n = 1, Co(III) → Co(II).

Compound	$E_{1/2}$, v. *vs.* S.C.E.		i_d, μa.			$\frac{i_d}{m^{2/3}t^{1/6}}$
	1st wave[a]	2nd wave[a]	1st wave[a]	2nd wave[a]	Total	
Isomers containing two negative groups						
cis-Dinitrotetramminecobalt(III) chloride	−0.05				2.84 at −0.730 v.	1.69
trans-Dinitrotetramminecobalt(III) chloride	− .21				2.96 at −0.489 v.	1.77
cis-Dinitrobisethylenediaminecobalt(III) nitrate[c]	− .24	−0.41	2.10	0.70	2.80 at −0.564 v.	1.66
trans-Dinitrobisethylenediaminecobalt(III) nitrate[c]	− .27	− .40	1.97	.88	2.85 at −0.555 v.	1.69
cis-Nitroisothiocyanatobisethylenediaminecobalt(III) chloride monohydrate[b,c]	− .04	− .38	2.15	.56	2.71 at −0.524 v.	1.62
trans-Nitroisothiocyanatobisethylenediaminecobalt(III) chloride monohydrate[b,c]	− .12	− .36	2.38	.44	2.82 at −0.602 v.	1.67
Isomers containing one or no negative group						
cis-Nitrobisethylenediamineamminecobalt(III) bromide[d]	−0.21	−0.40	1.86	0.93	2.80 at −0.566 v.	1.66
trans-Nitrobisethylenediamineamminecobalt(III) nitrate[e]	− .20	− .40	1.86	.90	2.76 at −0.558 v.	1.64
cis-Isothiocyanatobisethylenediamineamminecobalt(III) thiocyanate	− .13	− .39	1.00[g]	.94[g]	1.94[g] at −0.560 v.	
trans-Isothiocyanatobisethylenediamineamminecobalt(III) thiocyanate	− .10	− .39	1.59	1.23	2.82 at −0.582 v.	1.67
cis-Bisethylenediaminediamminecobalt(III) iodide	− .31				2.74 at −0.570 v.	1.63
trans-Bisethylenediaminediamminecobalt(III) chloride monohydrate[f]	− .31				2.84 at −0.578 v.	1.69

[a] Note that the terms "first wave" and "second wave" as used here both refer to the reduction step Co(III) → Co(II). [b] Supporting electrolyte: 0.1 M KNO_3. [c] Two drops of 0.1% methyl red per 100 ml. of solution added as a maximum suppressor. [d] Solution 0.002 M with respect to potassium nitrate. [e] Solution 0.002 M with respect to sodium bromide. [f] Solution 0.003 M with respect to potassium iodide. [g] Contaminated with potassium thiocyanate.

tential of −0.40 v. *vs.* S.C.E. (3) *cis*- and *trans*-dichlorobisethylenediaminecobalt(III) chlorides aquate easily in solution. Polarographic reductions of the aqueous solutions of each of these produced a wave at −0.40 v. using either 0.1 M potassium nitrate or 0.1 M potassium chloride as supporting electrolyte. The values obtained were the same if the solution was boiled before use. (4) Polarographic reduction of *cis*-hydroxoaquobisethylenediaminecobalt(III) bromide provided an additional check on the half-wave potential of an aquobisethylenediamine complex of the general type postulated. The reduction gave a half-wave potential of −0.40 v. *vs.* S.C.E. (5) A contaminant would not likely be the same for all compounds studied nor would it seem likely that different contaminants in the various compounds would happen to have the same half-wave potential—that is, −0.40 v. (6) Five successive recrystallizations of *cis*-dinitrobisethylenediaminecobalt(III) nitrate produced no change in polarographic behavior, giving a further indication that the second of the two waves observed was not due to a contaminant. (7) The relative heights of the two waves varied with different runs for a given compound but the total diffusion current for the two waves taken together was always the same, indicating the possibility of a relatively slow equilibrium in the aquation process. The concentration of each species would depend upon age of the solution but the total concentration of reducible ion would be a time invariant.

An independent supporting piece of evidence is that of Kivalo[27] who reports to us that he has obtained two waves for the Co(III) to Co(II) reduction step of trimethylenediaminebisethylenediaminecobalt(III) chloride in 0.1 M sodium nitrate. The second of the two waves occurred at −0.41 v. *versus* S.C.E.

Table I gives half-wave potentials and diffusion current constants for two waves for the Co(III) to Co(II) reduction of all the ethylenediamine complexes studied except the *cis*- and *trans*-bisethylenediaminediamminecobalt(III) ions. The polarograms for these two isomeric compounds give some indication of a double wave, too, but the second wave merges so closely with the first that separate evaluation is not practical.

The absence of a double wave for *cis*- and *trans*-dinitrotetramminecobalt(III) chloride does not seem unreasonable in view of the fact that coördination compounds containing ammonia are usually considerably less stable than the corresponding ethylenediamine derivatives. Aquation of the dinitrotetrammine compound undoubtedly involves replacement of ammonia molecules as well as of nitrite ions. Hence, aquation, once begun, would be more extensive than in the ethylenediamine compounds and the postulated equilibrium between the parent compound and a stable aquated complex would not pertain in the tetrammine case. *cis*-Dinitrotetramminecobalt(III) chloride decomposes on standing for several hours in dilute solution, with the formation of a precipitate of cobalt oxide. No such precipitate forms from *cis*-dinitrobisethylenediaminecobalt(III) nitrate under similar conditions.

In view of the evidence presented, it has been decided to regard the first wave, in those cases where two waves arise for the reduction step Co(III) to Co(II), to be that of the parent reducible

(27 Pekka Kivalo, University of Illinois, private communication.

TABLE II

POLAROGRAPHIC REDUCTION OF AMINO ACID DERIVATIVES

Supporting electrolyte: (a) 0.1 *M* KCl; (b) 25 ml. of 70.72% $HClO_4$ per 100 ml. of solution. m = 1.397 milligrams per second; n = 1, Co(III) → Co(II).

Compound	Concn., mole/l.	Supporting electrolyte	$E_{1/2}$, v. *vs.* S.C.E.	i_d, μa.	$\frac{i_d}{m^{2/3}t^{1/6}}$
α-Triglycinecobalt(III) dihydrate	0.001	(a)	−0.04	2.78 at −0.232 v.	1.63
β-Triglycinecobalt(III) monohydrate	Almost saturated	(a)	− .03		
α-Triglycinecobalt(III) dihydrate	0.001	(b)	+ .04	2.24 at −0.230 v.	1.35
β-Triglycinecobalt(III) monohydrate	.001	(b)	+ .04	2.28 at −0.299 v.	1.37
α-Trisalaninecobalt(III)	.001	(b)	− .08	1.83 at −0.360 v.	1.10
β-Trisalaninecobalt(III)	.001	(b)	− .07	1.96 at −0.299 v.	1.15

ion and to assume that the wave at about −0.40 v. is that of an aquated form in equilibrium with the parent ion. In view of the acidic properties of the diaquobisethylenediaminecobalt(III) ion, the aquated species may actually be a hydroxo complex of some type.

An examination of Table I shows that the half-wave potentials for the first wave of the compounds containing negative groups in two of the coördination positions and neutral groups in the other four are more positive for the *cis* isomers, indicating easier reduction, than for the corresponding *trans* isomers. This is the result expected from our earlier work[4] which dealt only with *cis*- and *trans*-dinitrotetramminecobalt(III) chloride. In this type of compound, a dipole exists within the coördination sphere of the *cis* form but not in that of the symmetrical *trans* isomer.

Since little is known concerning the mechanism of the electroreduction of complex inorganic ions at the dropping mercury electrode, a completely adequate explanation for this result is difficult to formulate. It seems reasonable to assume, however, that a *cis* complex which contains two negative groups and four neutral groups should, by virtue of the mutual electrostatic repulsion of these adjacent centers of electronegativity, be generally less stable than the symmetrical *trans* isomer. This would be expected to lead to more positive half-wave potentials for the *cis* isomer.

Table I indicates that those compounds which contain only one or no negative groups in the coördination sphere—hence possessing about the same internal dipole in both the *cis* and *trans* isomer or no appreciable internal dipole, respectively—do not show easier reduction on the part of the *cis* isomer. *cis*-Nitrobisethylenediamineamminecobalt(III) bromide and *cis*-isothiocyanatobisethylenediamineamminecobalt(III) thiocyanate, in fact, show slightly more difficult reduction than the corresponding *trans* isomers with a difference in half-wave potential of 0.01 and 0.03 v., respectively. The *cis*- and *trans*-bisethylenediaminediamminecobalt(III) compounds appear to be reduced with equal ease.

Diffusion current constants are given for the total current observed in the two waves for the Co(III) to Co(II) reduction step of each compound except *cis*-isothiocyanatobisethylenediamineamminecobalt(III) thiocyanate which was known to be contaminated with potassium thiocyanate. The relative rates of diffusion of the *cis* ions in Table I tend to be slightly lower than those of the corresponding *trans* isomers. The decrease in diffusion current constants on proceeding downward in the first section of Table I for either the *cis* isomers or the *trans* isomers can probably be attributed to a corresponding increase in the size of the reducible species.

Maxima, observed in the polarograms of *cis*- and *trans*-dinitrobisethylenediaminecobalt(III) nitrate and *cis*- and *trans*-nitroisothiocyanatobisethylenediaminecobalt(III) chloride monohydrate, were suppressed by the addition of methyl red.

Tenth molar potassium chloride was ordinarily employed as a supporting electrolyte. In some cases where the wave for the complex tended to merge with the anodic wave for mercury, 0.1 *M* potassium nitrate was used to move the mercury wave to a more positive potential. *cis*-Nitrobisethylenediamineamminecobalt(III) bromide and *trans*-nitrobisethylenediamineamminecobalt(III) nitrate were made 0.002 *M* with respect to potassium nitrate and 0.002 *M* with respect to potassium bromide, respectively, to ensure that both isomeric ions were reduced in identical media. The same reason accounts for the solution of *trans*-bisethylenediaminediamminecobalt(III) chloride monohydrate being made 0.003 *M* with respect to potassium iodide.

Table II concerns the isomeric glycine chelates and the isomeric alanine chelates of cobalt. The glycine isomers were studied in both neutral and acid aqueous solutions, although one isomer was not soluble to the extent of 0.001 *M* in the neutral solvent. The insolubility of both alanine derivatives in water made it necessary to study them in acid solution only. Very little difference is noted in the polarographic behavior of any two corresponding isomers when the same solvent is used. The differences observed in the behavior of the triglycine compounds on changing from a neutral to an acid solvent, however, suggest further work on the effect of *p*H on the polarographic reduction of these compounds. The more negative half-wave potentials for the alanine compounds, as compared with the corresponding glycine derivatives, can probably be attributed to extra stability of the coördinate covalent linkages to cobalt imparted by the additional methyl group on alanine.

The possibility of distinguishing between *cis* and *trans* isomers polarographically in the absence of supporting electrolyte was studied. Without supporting electrolyte, the migration current is a significant part of the limiting current. A *cis* ion containing two negative groups and four neutral groups might by virtue of its internal dipole be oriented in the unsymmetrical field around the dropping mercury electrode and thereby migrate to the electrode at a different rate than the symmetrical *trans* form. It follows that the migration current, and hence the limiting current, would be different for the *cis* ion than for the *trans*.[28]

The situation in the absence of supporting electrolyte is complicated by the formation of electrolyte (nitrite ions, for example) during the reduction, as well as by stirring effects associated with maxima which may not completely disappear even at more negative potentials. Absolute values for limiting currents are, therefore, not reproducible. Experimentally, the *cis*-dinitrotetramminecobalt(III) chloride has consistently given slightly higher limiting current values than the corresponding *trans* isomer in the absence of supporting electrolyte. The *trans* isomers of dinitrobisethylenediaminecobalt(III) nitrate and nitroisothiocyanatobisethylenediaminecobalt(III) chloride monohydrate have shown higher limiting currents than the corresponding *cis* forms.

It is apparent that difficulties inherent in the experimental method for study in the absence of supporting electrolyte may make the polarograph inadequate to measure accurately the differences in migration current which the theory suggests. On the basis of the present work, therefore, it is felt that polarographic reductions in the presence of supporting electrolyte show more promise in serving as an aid to differentiation between certain *cis* and *trans* isomers in solution.

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[28] H. F. Holtzclaw, Jr., Ph.D. Thesis, University of Illinois, 1947.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF CALIFORNIA]

Measurement of Disproportionation Rates at the Dropping Mercury Electrode

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A theoretical study has been made of current increases at the dropping mercury electrode arising from disproportionation of the electrode product. A relationship is derived between this current increase, the diffusion current and the disproportionation rate constant, which reduces to a particularly simple form for small rates and depolarizer concentrations. In this case the rate constant is shown to be proportional to the slope of the plot i/i_d *vs.* i_d, where i is the observed limiting current and i_d the current due to diffusion alone. These conclusions were tested on the reduction of U(VI) to unstable U(V) in chloride and perchlorate solutions. Quantitative agreement with the theory was found in all the points tested with the exception of an anomaly observed in strongly acid chloride solutions. The experiments indicated that the theory permits the identification of a second-order reaction involving the electrode product, the discovery of the role of other ions in the reaction mechanism, and an estimate of the magnitude of the second-order disproportionation rate constant.

Introduction

At the dropping mercury electrode (d.m.e.) in acid solution, uranium(VI) is reduced to uranium (V) at potentials between −0.17 and −0.9 v. *vs.* the saturated calomel electrode (S.C.E.).[2] U(V) is unstable and disproportionates into U(VI) and U(IV) according to the rate law[3]

$$\frac{dU(V)}{dt} = -k'(H^+)(U(V))^2 \qquad (1)$$

A portion of the U(VI) from the disproportionation reaches the electrode and is reduced. The limiting current therefore has a reaction-controlled as well as a diffusion-controlled component. The increase in current beyond that corresponding to a one-electron diffusion-controlled reduction is a function of the rate of disproportionation.[2] In this paper a theoretically derived relationship between limiting current and the second-order rate constant has been sought, that is generally applicable to the case in which the primary electrode product is an oxidation state unstable with respect to disproportionation. The theory has been tested experimentally by applying it to the reduction of uranyl ion in acid solution. Since the formation of unstable intermediates at the d.m.e. is often postulated, the results obtained in this paper may be of use in permitting an estimate of the associated disproportionation rates. Related problems involving first-order reactions at the d.m.e. have been treated with varying degrees of rigor by Brdička[4] and co-workers, and Delahay.[5]

Theoretical

The Simultaneous Reaction and Diffusion Problem.—In this paper we are considering an electrode process of the type

$$A + ne^- \longrightarrow B \text{ or } A \longrightarrow B + ne^- \qquad (2a)$$

$$2B \longrightarrow A + C \qquad (2b)$$

where C is an oxidation state which does not depolarize the electrode at the potential in question. The second reaction is second order with respect to B.

When the depolarizer concentration is affected by the decomposition of the electrode product, a reaction rate term must be included in the diffusion equations of species A and B, since the change of concentration with time is not dependent on diffusion alone. In our case the term involves the electrode product concentration, which must be solved for simultaneously.

Accordingly one arrives at the equations

$$\begin{aligned}\frac{\partial A}{\partial t} &= D_a \frac{\partial^2 A}{\partial x^2} + {}^1/_2 kB^2 \\ \frac{\partial B}{\partial t} &= D_b \frac{\partial^2 B}{\partial x^2} - kB^2\end{aligned} \qquad (3)$$

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